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Lutetium Oxide Coatings by PVD

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Abstract

Due to its high density and cubic structure, Lutetium oxide (Lu_2O_3) has been extensively researched for scintillating applications. Present manufacturing methods, such as hot pressing and sintering, do not provide adequate resolution due to light scattering of polycrystalline materials. Vapor deposition has been investigated as an alternative manufacturing method. Lutetium oxide transparent optical coatings by magnetron sputtering offer a means of tailoring the coating for optimum scintillation and resolution. Sputter deposited coatings typically have inherent stress and defects that adversely affect transparency and emission. The effect of process parameters on the coating properties is being investigated via x-ray diffraction (XRD), scanning electron microscopy (SEM) and emission spectroscopy, and will be presented and discussed.

INTRODUCTION

Rare earth oxides have been extensively used in the x-ray detector industry for quite some time due to their stability, high density and high atomic number [1]. However, they have generally been limited to small area detectors due to manufacturing limitations. Lutetium Oxide (Lu_2O_3) doped with Europium Oxide (Eu_2O_3) has been studied using hot pressing and sintering as an alternative to the industry standard Cesium Iodide doped with Tantalum (CsI:Tl). In terms of optical and scintillating properties, CsI:Tl has a good transparency, density of 4.51g/cc and emits ~60,000 photons per MeV of incident x-rays [2]. Compared to $\text{Lu}_2\text{O}_3\text{:Eu}^{3+}$, which has a highly transparent BCC structure, a density of 9.4g/cc and emits ~30,000 photons per MeV [1]. High density and high atomic number of Lu_2O_3 makes it an ideal scintillator. A viable manufacturing process would expand its market to the large area scintillators.

Current manufacturing methods, such as sintering and hot pressing produce a transparent 2–3mm thick disc that must be ground and polished to a thickness close to the desired thickness. It must then be pixelized into 20 μm by 20 μm square pixels as shown in Figure 1 using a highly labor intensive laser ablation process to reduce light scattering. The top surface is then placed on the CCD camera using optical glue and the back is ground off. [2] Dentistry is one of the applications for such a device and requires approximately 200 microns of Lu_2O_3 , compared to 2mm for CsI , to absorb most of the incoming x-rays. Our proposal is to develop vapor deposited Lu_2O_3 coatings as an alternative manufacturing method that would enable largescale detector fabrication.

EXPERIMENT

The radio frequency (R.F.) magnetron sputtering setup used had a 2 inch diameter target angled at 45 degrees with respect to the substrate. The target was made by hot pressing Lu_2O_3 powder doped with 5 mol% Eu_2O_3 at 1700°C using a graphite uniaxial hot press. A thin 2 inch diameter graphite disc was used as the substrate and it was rotated at approximately 20rpm to increase uniformity. The R.F. power source was an Advanced Energy RFX600 capable of producing 600 Watts.

Coatings were deposited at 50, 75 and 100 Watts and examined. It was determined that 100 Watts was the maximum useable power level, above which charging and target damage occurs. The coatings were examined using a Bruker D8 Focus X-ray diffraction (XRD) unit using Cu-K α radiation to determine orientation, and a Zeiss field emission scanning electron microscope (SEM) to examine the microstructure. All coatings were heat post-treated in a Tungsten furnace at 900°C in an argon atmosphere for 2 hours.

DISCUSSION

Microstructural analysis of the top surface and the fractured cross sections, as shown in Figure 2, revealed a strong morphological dependence on input power. The surface images showed a clear transition from what appears to be cellular growth to plate growth. We are further investigating the growth using transmission electron microscopy (TEM) to fully characterize the growth mechanism. At 50W and 100W the columnar growth appears to be of uniform width and perpendicular to the surface, whereas at 75W, the columnar growth becomes radial. The diameter of the columnar growth is not clear from the fractured cross section. However, with top surface images in figure 2, clearly show larger boundaries, indicative of a columnar grain growth. As expected, grain diameter measurements indicated a trend of decreasing columnar diameter with increasing power (or deposition rate) as shown in Table 1.

The columnar growth was determined to be (100) textured for low input power and (111) textured for high input power as determined from the XRD pattern (Figure 3). It is noteworthy that the intensities of the (100) and (111) peaks are low, indicating that crystallinity/orientation is not significant. Low intensity diffraction peaks from other planes further suggest that not all growths are perpendicular and potentially slightly polycrystalline. This is most likely a result of slow kinetics because the low thermal energy does not enable the newly formed grains to grow epitaxially. Furthermore, all the XRD patterns are increasingly shifted towards a larger unit cell with increasing power, which is typically attributed to growth stresses. The $\langle 100 \rangle$ is a lower energy growth direction and with sufficient stresses can induce a shift towards $\langle 111 \rangle$ growth.

In a PVD sputtering system, the plasma intensity is dependent on the power applied, which also affects the sputtering rate. The plasma itself can attain high temperatures and can provide some thermal energy to the coating and the substrate can reach temperatures up to 100°C. However, the plasma provides a relatively large amount of thermal energy to a very thin layer, notably the deposition layer. This is believed to be the reason for the drastic change in coating morphology observed at 75W. At this power there is a balance between deposition rate and thermal energy provided by the plasma that enables better crystallization. At 50W the low intensity plasma provides low thermal energy and despite reduced deposition rates, is not adequate for crystalline growth. At 100W, despite increased plasma thermal energy, the atoms do not have sufficient time to rearrange because of the higher density of incoming atoms.

Heat Treatment Analysis

The samples were then heat treated to increase crystallinity and observe changes in morphology. As seen in figure 4, the (100) peak has reverted back to the theoretical position indicating stress relief. However, associated with the restored unit cell is a subsequent volume change resulting in reduced thickness and cracking (Figure 4). In the 100W case, the volume distortion leads to loss of adhesion making further analysis on the heat treated sample almost impossible. One can observe in Figure 4 that the morphology of the coating remains identical to the as-deposited coating indicating the coating stability. A small increase in the intensity of the (100) peak was observed indicating slight grain growth or increase in crystallinity. In figure 5 it can be seen that the edge of the 100W sample remains adherent, which can be attributed to the non-uniformity of deposition conditions. In magnetron sputtering, a ring source is created

which in our case is angled at approximately 45 degrees to a rotating substrate. The angling and rotation is used to improve thickness uniformity but results in non-uniform plasma heating and deposition angles which are critical growth factors. Furthermore, the kinetic energy of the ejected material plays a crucial role in the coating properties and is a function of the travel distance and total pressure. Therefore, the center of the substrate will be exposed to relatively constant deposition conditions, whilst the outer edges will vary significantly every half rotation. XRD pattern of the outer edge is that of a partially polycrystalline coating.

One of the indicators of the extent of crystallization in a scintillating material is the emission intensity and spectrum. The emission spectrum of the 'as deposited' and heat treated samples were measured using cathodoluminescence. The 'as deposited' emission intensity was found to be too low to be detected whilst the heat-treated samples appeared to have a standard emission spectrum. Ultraviolet light at 254 nm also induces emission due to the charge transfer band at approximately 250nm in the host material [4] as seen in Figure 5. The lack of emission can be attributed to either low crystallinity or a large number of defects that act as charge traps resulting in non-radiative transitions. Once heat-treated, the defects are mostly eliminated and increased crystallinity results in improved emission. The 75W sample produced the highest emission intensity, further confirming the previously reported results.

CONCLUSIONS

RF magnetron sputtered coatings of $\text{Lu}_2\text{O}_3:\text{Eu}^{3+}$ were successfully deposited using vapor deposition. The as-deposited coatings were partially crystalline and did not scintillate. Thermal treatment of the coatings resulted in increased crystallinity and lower defects, leading to excellent scintillation. The columnar nature of the coatings potentially makes this a very attractive candidate for use in x-ray imaging, eliminating the need for the highly labor intensive laser pixelization process.

Acknowledgments

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Figure 1.
Top surface scanning electron image of a laser pixelized Lutetium Oxide ceramic. [2]

Figure 2. Effect of power on coating morphology and growth rates. The fractured cross section images and their respective surface morphologies have been shown.

Figure 3. X-ray diffraction patterns of the as deposited coatings. Highest intensity peaks have been magnified and peak shift has been emphasized.

Figure 4. X-ray diffraction pattern of the (100) peak to emphasize stress reduction. On the left: low magnification image of the top surface. On the right: high magnification image of the top surface.

Figure 5. Ultraviolet (254nm) light excitation of the coatings. Left half: as deposited. Right half: heat treated. Input power: (a) 50W (b) 75W (c) 100W.

Table I

X-ray diffraction analysis compared with SEM grain size measurements

Power (Watts)	Measured Grain Size (nm)	Lattice Distortion	Volume Distortion
50	415	1.0%	3.0%
75	290	1.2%	3.6%
100	247	2.1%	6.3%